LA-UR –91-1666

-- c,

TITLE: VIBRATIONAL SPECTROSCOPY OF SHOCK-COMPRESSED LIQUID CO

AUTHORS(S): D.S.MOORE, S.C.SCHMIDT, M.S.SHAW, AND J.D.JOHNSON

DISCLAIMER

Los Alamos

Los Alamos National Laboratory
Los Alamos New Mexico 87545

VIBRATIONAL SPECTROSCOPY OF SHOCK-COMPRESSED LIQUID CO[a)]

D. S. Moore, S. C. Schmidt, M. S. Shaw, and J. D. Johnson

Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Single-pulse, multiplex, coherent anti-Stokes Raman spectroscopy (CARS) was used to observe the vibrational spectra of liquid CO shock compressed to several pressures and temperatures up to 9.9 GPa and 2010 K. The experimental spectra were compared to synthetic spectra calculated using a semiclassical model for CARS intensities and estimated vibrational frequencies, peak Raman susceptibilities and Raman line widths. A comparison of these data with results in the isoelectronic and materially very similar N_2 show a significant difference in vibrational frequency shift with pressure.

INTRODUCTION

The molecular-level physical and chemical properties of small molecules at high densities and temperatures are of considerable importance to the detailed understanding of the behavior of the unexpanded products of detonations. Carbon monoxide is likely to be a major constituent of such reacted high explosives. CO is isoelectronic with nitrogen, has a very similar boiling point (81.5 vs 77 K) and liquid density (0.793 vs 0.808 g/cm^3), and has essentially the same Hugoniot up to 10 GPa[1-3]. We have recently reported coherent anti-Stokes Raman spectroscopy (CARS) measurements of the vibrational frequency, third order susceptibility, and vibrational linewidth of shock-compressed liquid nitrogen.[4-6] We report here similar measurements in shock-compressed liquid carbon monoxide that were performed in order to obtain detailed molecular level information on the CO equation of state, as well as to investigate what influence the inter- and intra-molecular potentials in two very similar molecules have on the pressure and temperature dependence of their vibrational spectra.[7]

The high-pressure/high-temperature states of liquid CO investigated in this study were achieved by the dynamic compression technique and the vibrational spectra were recorded using CARS. The experimental apparatus has been described previously.[8-11] Briefly, a projectile launched by a two-stage light-gas gun dynamically compressed a liquid CO sample that had been condensed into a cryogenic target

assembly. The target was designed to reflect CARS signals from a highly polished 304 stainless steel target plate at the front through a 6.3 mm-diameter lithium fluoride window at the rear. Single-shock velocities were measured to better than 2 percent and the initial pressure and temperature of the liquid CO sample were determined to $\pm$0.7 kPa and $\pm$2 K, respectively. Initial sample densities were taken from Vargaftik.[12] The CO samples were condensed from gaseous CO (purity > 99.5%).

CARS[13] is a parametric process in which three waves, two at a pump frequency and one at a Stokes frequency, are mixed in a sample to produce a coherent beam at the anti-Stokes frequency. The efficiency of this mixing is greatly enhanced if the difference in frequency between the pump and Stokes coincides with the frequency of a Raman active mode of the sample. A previously described[4] semiclassical model was used to calculate synthetic CARS spectra that matched the experimental data. In these experiments, a Nd:YAG laser was used to pump the two dye lasers that generate the CARS signal, one being a broad-band "Stokes" laser (627-645 nm) and the other a narrow-band "pump" laser operated near 562 nm. Multichannel detection of the CARS signals was done using an intensified photodiode array (Tracor Northern 6132) and analyzer (Tracor Northern 6500) gated on for 20 ns (Tracor Northern TA-6130-2) at the expected arrival time of the CARS signals. In addition, the broad-band dye laser spectral profile was measured in each experiment using another 1 m spectrometer and a photodiode array (EG&G Reticon 512S). Wavelength calibrations were all done using vacuum wavenumbers of atomic emission lines.[14]

Shock pressures, densities, and temperatures were calculated using an effective spherical potential that has been shown to accurately reproduce both nonspherical molecular dynamics simulations and experimental Hugoniot and brightness temperature data.[15-17] Doubly shocked states were inferred from impedance matching of the CO shock, at the measured shock velocity, reflecting off the known window material assuming the theoretical equation of state

for carbon monoxide. The equation-of-state parameters for lithium fluoride are from published data.[18] Based on the previously stated experimental errors, estimated uncertainties in pressure are ±1 GPa for the principal Hugoniot measurements and and ±2 GPa for the reflected shocks. These uncertainties are dominated by the experimental uncertainty in the shock velocity.

We have obtained[7] CARS spectra of fluid CO at many shock pressures and temperatures up to 9.9 GPa and 2010 K (single shock), and 6.5 GPa and 620 K (reflected shock) (e.g. Fig. 1). Because of timing constraints, some spectra (e.g. Fig. 1a) were obtained when the shock wave had not yet reached the window, resulting in CARS signals being generated in both singly-shocked and ambient liquid CO. Other spectra (e.g. Fig 1b) were obtained when the shock had reflected from the window back into the sample, resulting in CARS signals from both singly and doubly shocked CO. The frequency shift with shock pressure is sufficiently small in CO that there is not a clear separation between the fundamental vibrational transition in the ambient liquid and in the singly-shocked liquid. At the higher shock pressures, the hot-band vibrational transitions become observable (as in Fig 1a). All of the spectra in this paper were filtered using a Cooley-Tukey fast Fourier transform algorithm and low-pass Gaussian filters ranging from 0.12, .12 cm to 0.30, 0.30 cm.[19]

Above about 10 GPa single shock, the samples experienced a very rapid decrease in transmissivity, as measured by a helium-neon laser beam that traverses a path similar to the CARS beams.[19] In addition, CARS signals were not obtained for any of these strongly-shocked samples. This result implies that the difficulty in recording CARS spectra of shocked CO above 10 GPa is related to a large sample absorptivity. It is interesting that the region above 10 GPa is also the pressure range where a nonreactive CO equation-of-state curve ceases to fit the experimental shock data points.[1]

Estimated vibrational transition frequencies, susceptibility ratios, and linewidths were used to compute

synthetic CARS spectra, which were then convolved with the 3.5 cm^{-1} FWHM spectrometer slit function. The adequacy of the fit of these calculated spectra to the experimental data was judged primarily by visual inspection. Representative spectral fits are shown in Fig. 1 by the dashed curves.

Figure 2 shows the Raman shifts extracted from the best fit calculated spectra versus shock pressure for the fundamental transition. Both the singly and doubly shocked materials show a monotonic increase of the vibrational frequency with increasing shock pressure up to the highest pressure studied. It is interesting to note the effect of temperature in these data. When the fluid is singly or doubly shocked to the same density, the difference in measured Raman shift is due to the effects of temperature on the potential and on the portion of the potential sampled on average. The measured Raman frequency shifts for ambient, singly shocked and doubly shocked CO were least squares fit to an empirical function of pressure and temperature.[7] The short line segment near each data point in Fig. 2 gives the calculated frequency value predicted by the function at the measured pressure and temperature, and the long curves show the positions of the 500, 1000, and 2000 K isotherms also obtained using the function. Each isotherm is drawn over the approximate range of validity of the empirical fit.

The Raman shift with shock pressure measured in CO is dramatically smaller than what was observed previously in shock-compressed N_2.[4-6] For comparison, the dashed curve in Fig. 2 is the 1000 K isotherm obtained in N_2.[6] This considerable difference is surprising because of the previously noted similarities between CO and N_2 -- their similar boiling points and liquid densities, the fact that they are isoelectronic, and their essentially identical Hugoniots up to 10 GPa. Their different vibrational frequency shifts indicate significant differences in the details of their inter and intramolecular potentials. The presence of a permanent dipole in CO has been used to explain the much larger Raman linewidth in ambient liquid CO versus N_2.[20] Other authors have noted the perturbation of vibrational

frequencies and line broadening due to molecular interactions.[21] Similar effects may also be operative in the observed anomalously small vibrational frequency shift of CO.

Using the susceptibilities and linewidths extracted from the spectral fits and the techniques of Refs. 4-6, it was found that the spectra are adequately represented assuming Boltzmann equilibrium of the vibrational levels. Similarly to the comparable result in shocked liquid N_2, this result implies that energy has been transferred from the bulk translational motion into the vibrational energy levels in a time less than or comparable to the characteristic time of the shock-compression experiment of ~ 10 ns.

In summary, at single shock pressures up to 9.9 GPa, carbon monoxide exists as a molecular fluid whose vibrational frequency increases with pressure. The frequency increase observed was substantially less than that observed previously in nitrogen, implying a significant difference in the details of their inter- and intramolecular potentials. An empirical fit showed that the Raman frequency shifts could be accurately described with linear pressure and temperature dependences. The measured intensities and linewidths of the Raman transitions suggest that thermal equilibration of the vibrational levels is achieved in less than 10 ns.

ACKNOWLEDGEMENT

REFERENCES

1. W. J. Nellis, F. H. Ree, M. van Thiel, and A. C. Mitchell, J. Chem. Phys. **75**, 3055 (1981).

2. M. Ross and F. H. Ree, J. Chem. Phys. **73**, 6146 (1980).

3. M. S. Shaw and J. D. Johnson, in **Int'l Detonation Symposium, 8th,** (Albuquerque, NM, 1985) (NSWC MP86-194, Silver Spring, MD) p. 198.

4. S. C. Schmidt, D. S. Moore, and M. S. Shaw, Phys. Rev. B **35**, 493 (1987).

5. D. S. Moore, S. C. Schmidt, M. S. Shaw, and J. D. Johnson, J. Chem. Phys. **90**, 1368 (1989).

6. S. C. Schmidt, D. Schiferl, A. S. Zinn, D. D. Ragan, and D. S. Moore, J. Appl. Phys. **69**, 2793 (1991).

7. D. S. Moore, S. C. Schmidt, M. S. Shaw, and J. D. Johnson, submitted to J. Chem. Phys. 1991.

8. D. S. Moore, S. C. Schmidt, and J. W. Shaner, Phys. Rev. Lett. **50**, 1819 (1983).

9. S. C. Schmidt, D. S. Moore, and D. Schiferl, M. Châtelet, T. P. Turner, J. W. Shaner, D. L. Shampine, and W. T. Holt, in **Advances in Chemical Reaction Dynamics,** P. M. Rentzepis and C. Capellos, Eds. (D. Reidel, Dordrecht, 1986), p. 425.

10. D. S. Moore and S. C. Schmidt, in **Shock Waves in Condensed Matter - 1987,** edited by S. C. Schmidt and N. C. Holmes, (North-Holland, Amsterdam, 1988), p. 35.

11. S. C. Schmidt, D. S. Moore, M. S. Shaw, and J. D. Johnson, in **Shock Waves in Condensed Matter - 1987,** edited by S. C. Schmidt and N. C. Holmes, (North-Holland, Amsterdam, 1988), p. 489.

12. N. B. Vargaftik, **Tables on the Thermophysical Properties of Liquids and Gases,** (Hemisphere, Washington, 1975),p. 154.

13. W. M. Tolles, J. W. Nibler, J. R. McDonald, and A. B. Harvey, Appl. Spectrosc. **31**, 253 (1977).

14. **M. I. T. Wavelength Tables,** prepared by F. M. Phelps III (MIT Press, Cambridge, MA, 1982), Vol. II.

15. M. S. Shaw, J. D. Johnson, and B. L. Holian, Phys. Rev. Letters **50**, 1141 (1983).

16. J. D. Johnson, M. S. Shaw, and B. L. Holian, J. Chem. Phys. **80**, 1279 (1984).

17. M. S. Shaw, J. D. Johnson, and J. D. Ramshaw, J. Chem. Phys. **84**, 3479 (1986).

18. S. P. Marsh, **LASL Shock Hugoniot Data** (University of California Press, Berkeley, CA, 1980).

19. S. C. Schmidt, D. S. Moore, M. S. Shaw, and J. D. Johnson, J. Chem. Phys. **91**, 6765 (1989).

20. S. R. J. Brueck, Chem. Phys. Letters **53**, 273 (1978).

21. S. A. Akhmanov, F. N. Gadjiev, N. I. Koroteev, R. Yu. Orlov, and I. L. Shumay, Appl Opt. **19**, 859 (1980).

FIGURE. 1
Experimental and computed representative CARS spectra of shock-compressed liquid CO. The solid curves are the experimental data and the dashed curves are computed synthetic spectra.

FIGURE 2
Raman shift of the fundamental vibration vs pressure. • single shock; ○ double shock; — CO isotherms; - - - N_2 isotherm.

a)

Intensity (Arb. Units)

$P_1 = 0.00018$ GPa
$P_2 = 6.90$ GPa

Raman Shift (1/cm)

b)

Intensity (Arb. Units)

$P_1 = 2.46$ GPa
$P_2 = 5.96$ GPa

Raman Shift (1/cm)